



Exceptional visible-light activities of g-C₃N₄ nanosheets dependent on the unexpected synergistic effects of prolonging charge lifetime and catalyzing H₂ evolution with H₂O

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ABSTRACT

It is highly desired to develop an efficient g-C₃N₄-based photocatalyst for energy production under visible-light irradiation. Herein, it is shown that the optimized g-C₃N₄ nanosheet-based photocatalyst could exhibit exceptional photocatalytic activities for H₂ evolution under visible-light irradiation, by ~14-time improvement compared to that of bare g-C₃N₄ one. It is confirmed by the methods of transient-state surface photovoltage responses, transient-state PL spectra and electrochemical measurements that the exceptional photocatalytic activities are attributed to the unexpected synergistic effects of prolonging the charge lifetime and catalyzing H₂ evolution by coupling nanocrystalline anatase TiO₂ as a proper-energy platform to accept visible-light-excited electrons from g-C₃N₄ and by decorating a nano-sized noble metal as the co-catalyst respectively. Among three decorated noble metals (Ag, Au and Pt), to prolong the photogenerated charge lifetime is much meaningful for the used noble metal cocatalyst with weak catalytic function like Ag in H₂ evolution. Using nanocrystalline SnO₂ to replace TiO₂ is also applicable for the synergistic effect. Moreover, it is clarified by the designed experiment on photocatalytic CO₂ conversion to CD₄ in the presence of methanol in D₂O that the resource of evolved H₂ is mainly from the adsorbed H₂O other than the disassociated H⁺ from methanol.

1. Introduction

Hydrogen is abundant in our environment and widely stored in water (H₂O), hydrocarbons (such as methane, CH₄), and other organics [1–4]. One of the challenges on using H₂ as a fuel comes from efficiently extracting it from these compounds. Photocatalytic technique provides a promising way to produce H₂ fuel by utilizing solar energy [5–9]. Especially, visible-light-driven photocatalysts are attractive since they can utilize the visible-light as the main part of solar energy (46%) [10]. Among various narrow-bandgap photocatalysts investigated in recent years, graphitic carbon nitride (g-C₃N₄) has drawn tremendous scientific attention for photocatalytic H₂ evolution due to its several advantages of visible-light absorption, cheapness, high chemical and thermal stability, suitable valence band (VB) and conduction band (CB) position [11,12]. Notably, its CB bottom is rather negative (−1.3 eV vs NHE) so that its photogenerated electrons would possess enough energy to induce the reduction reactions for H₂ evolution thermodynamically [13,14]. However, the photocatalytic activity of g-C₃N₄ is still too low

to support its practical applications. This is usually attributed to the fast recombination of photogenerated electron-hole pairs and the lack of catalytic functions of separated electrons [15,16]. Thus, it is highly desired to develop a feasible method to enhance the separation of photogenerated charges and to provide strong catalytic functions for efficient visible-light photocatalysis on g-C₃N₄ to produce H₂.

Several attempts have been explored to enhance the charge separation of g-C₃N₄, including to construct a novel nanostructure, to couple another semiconductor and to decorate a noble metal, especially for the late ones [17–19]. Over the years, coupling a wide bandgap oxide, such as TiO₂ and SnO₂, to improve the H₂ evolution activity of g-C₃N₄ has been widely researched [14,20]. It is well accepted that the improved photoactivities are attributed to the promoted charge transfer so as to greatly prolong the charge lifetime. However, the apparent photoactivity is still unsatisfactory. This is because of the lack of catalytic functions for the transferred electrons to induce reduction reactions. Besides, another effective strategy is to only decorate a noble metal such as Pt, Au and Ag on the surface of g-C₃N₄ [21–23]. In this

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case, the modified noble metal could accept the photogenerated electrons so as to prolong the charge lifetime, simultaneously acting as the co-catalyst to provide the catalytic function for electron-induced reduction reactions. This is well responsible for the obviously improved photocatalytic activities of g-C₃N₄ for H₂ evolution after decorating a noble metal. By comparison, it is naturally deduced that to modify with a noble metal is much feasible for efficient photocatalysis on g-C₃N₄ compared with a wide bandgap oxide.

As for the modified noble metal, it is understandable that it could accept the photogenerated electrons from g-C₃N₄ since it possesses a rather low Fermi energy level. However, it is not quite beneficial to prolong the lifetime of transferred electrons with enough thermodynamic energy. This would make the photoactivity improvement to be limited to a certain degree, and it is different for different noble metals [24]. However, those are usually neglected since seldom related works have been reported to date. In addition, it should be pointed out that it is much favorable for the transferred electrons with enough thermodynamic energy to prolong the charge lifetime of g-C₃N₄ by coupling a wide bandgap oxide like TiO₂. Naturally expected, this will facilitate the transferred electrons to initiate the reduction reactions if a noble metal is used as the cocatalyst. Thus, it is assumed that there is a synergistic effect of prolonging the proper-energy electron lifetime and providing the catalytic functions to evolve H₂ on efficient photocatalysis of g-C₃N₄. Obviously, it is much meaningful to clarify the assumption for developing a highly efficient g-C₃N₄-based photocatalyst to produce solar fuels.

Based on the above consideration, it is much feasible to improve the visible-light photocatalytic activity of g-C₃N₄ by simultaneously coupling a wide bandgap oxide and decorating a noble metal. For the coupled oxide, anatase TiO₂ is chosen as the model semiconductor for it is a widely-used wide bandgap oxide, and its CB position is in proper energy level for H₂ evolution from water [25–27]. It is interesting to choose Ag as a model cocatalyst because it is a cheaper noble metal compared with Pt and Au, along with relative comparison investigation [28,29]. Moreover, it is necessary to deeply explore the photogenerated charge transfer and lifetime by employing different time-resolved photo-physical techniques like surface photovoltage response and photoluminescence (PL) spectra [25,30,31]. In addition, it is widely accepted that methanol is always used as the sacrificial agent to capture holes for efficiently photocatalytic H₂ evolution, simultaneously providing H⁺ [32,33]. Thermodynamically, it seems that it is much favorable for the disassociated H⁺ to evolve H₂ by photocatalysis, and some works suggest that the H⁺ provided by methanol oxidation will participate in the H₂ evolution process [33–35]. However, it is still disagreeable that the evolved H₂ mainly comes from the used H₂O or from the H⁺ provided by the methanol oxidation. Therefore, it is much meaningful to clarify the mentioned-above points from the scientific point of view in photocatalysis for energy production.

Herein, g-C₃N₄ nanosheet was firstly synthesized by the method of calcining urea, and then modified by coupling anatase-phase TiO₂ through a wet-chemical process and then by decorating a noble metal via a photodeposition method. It is shown that the optimized g-C₃N₄ nanosheet-based photocatalysts could exhibit exceptional photocatalytic activities for H₂ evolution under visible-light irradiation. It is confirmed that the exceptional photocatalytic activities are attributed to the usually-neglected synergistic effects of prolonging the charge lifetime and catalyzing H₂ evolution. Among the three used noble metals, the synergistic effect with the coupled TiO₂ for used Ag is much obvious, compared to those for Au and Pt, indicating that prolonging the photogenerated electron lifetime is much meaningful for the used Ag with weak catalytic function. Moreover, the designed D₂O isotope experiment for photocatalytic CO₂ conversion to CD₄ means that the evolved H₂ mainly originates from the adsorbed H₂O other than the disassociated H⁺ from methanol. This work provides a new physical insight on developing an efficient g-C₃N₄-based photocatalyst for energy production.

2. Experimental section

All the chemicals were of analytical grade and used as-received without further purification. Deionized water was used throughout the experiments.

2.1. Synthesis of g-C₃N₄

To prepare g-C₃N₄, in a typical process, 30 g of urea was taken and grinded into fine powder. Then the powder was transferred to a 100 mL aluminum crucible and treated in a muffle furnace at 550 °C (temp ramp 0.5 °C/min) for 3 h. After cooling to room temperature naturally, the product was grinded into fine powder prior to characterization.

2.2. Synthesis of TiO₂ nanoparticles

A sol-hydro-thermal method was employed to synthesize TiO₂ nanoparticles: 5 mL Ti(OBu)₄ was dissolved in 5 mL anhydrous ethanol, the solution was stirred for 30 min, denoted as solution A. 20 mL anhydrous ethanol, 5 mL water and 1 mL 70% HNO₃ were taken, then mixed and stirred for 30 min, denoted as solution B. Then solution A was added to solution B in a dropwise way under vigorous stirring condition at room temperature, and a yellowish transparent sol was obtained. Subsequently, 30.85 mL of the as-prepared solution was transferred into a Teflon-lined stainless steel autoclave and hydrothermally treated at 160 °C for 6 h. After cooling to room temperature naturally, the sample was centrifuged and washed three times with deionized water followed by absolute ethanol, and finally dried in air at 80 °C to obtain the TiO₂ precursor. TiO₂ nanoparticles were obtained by further treating TiO₂ precursor in a muffle furnace at 450 °C (temp ramp 10 °C/min) for 2 h.

2.3. Synthesis of TiO₂ coupled g-C₃N₄

1 g of the freshly prepared g-C₃N₄ was dispersed into a mixed solvent of 25 mL ethanol and 25 mL deionized water. Then different amounts (20, 40, 60 and 80 mg) of TiO₂ precursor were added into the solution and kept under vigorous stirring for 2 h. Then the samples were dried at 80 °C in the water bath under vigorous stirring. Finally, the samples were annealed at 450 °C (temp ramp 10 °C/min) for 2 h. The samples were denoted as xT/g-C₃N₄, in which the x indicates the mass ratio percentage of TiO₂ precursor to g-C₃N₄ in theory.

2.4. Synthesis of SnO₂ nanoparticles

SnO₂ was prepared by a hydrothermal method. In a typical process, 0.561 g SnCl₄·5H₂O was dissolved in 10 mL deionized water under continuous stirring for 1 h, denoted as solution A. 1.95 g sodium oleate (C₁₈H₃₃NaO₂) was dissolved in 10 mL deionized water and 20 mL acetic acid under continuous stirring for 1 h, denoted as solution B. The solution A was added dropwise into solution B, and the resulting emulsion was stirred for another 1 h. Finally, 30 mL of the emulsion was kept at 180 °C for 24 h in a Teflon-lined stainless-steel vessel and then cooled naturally to room temperature. Then the emulsion sequentially was washed with deionized water and absolute ethanol, followed by drying it at 80 °C in air to get SnO₂ precursor.

2.5. Synthesis of SnO₂ coupled g-C₃N₄

1 g of the freshly prepared g-C₃N₄ was dispersed into a mixed solvent of 25 mL ethanol and 25 mL deionized water. Then 60 mg SnO₂ precursor was added into the solution and kept under vigorous stirring for 2 h. Then the sample was dried at 80 °C in the water bath under vigorous stirring. Finally, the sample was annealed at 450 °C (temp ramp 10 °C/min) for 2 h.

2.6. Photodeposition of Ag nanoparticles

In a typical experiment, different amounts (the theoretical mole ratios of Ag to g-C₃N₄ were 0.1, 0.25, 0.4 and 0.5:100) of Ag nanoparticles were deposited on the g-C₃N₄ surface by the photo-deposition method. In the first step, the desired amount of silver nitrate (AgNO₃) and 1 g g-C₃N₄ were dispersed in a mixed solution of 50 mL methanol and 100 mL deionized water in a 250 mL beaker covered with a sealing film. Then the samples were treated by turns of sonication and stir, each for 10 min. After that, nitrogen gas was bubbled through the samples for 1 h to generate an inert atmosphere for the photodeposition of Ag nanoparticles. And then irradiated under a 300 W xenon lamp with a 420 nm cut-off filter for 3 h, under vigorous stirring. Finally, the samples were centrifuged and washed for three times with deionized water followed by absolute ethanol, and finally dried in air at 80 °C. The samples were denoted as yAg/g-C₃N₄, in which y means the mole ratio percentage of added Ag to g-C₃N₄ in theory. Particularly, to obtain g-C₃N₄ co-modified with noble metal and TiO₂ or SnO₂, the noble metal was photo deposited on TiO₂ or SnO₂ coupled g-C₃N₄.

2.7. Characterization

We took various techniques to characterize the prepared samples. The crystal structure was determined by of Bruker D8 Advance X-ray diffractometer equipped with graphite monochromatized Cu K α radiation with wave length equal to 1.54056 Å. For the X-ray diffraction measurement, the voltage was accelerated to 30 kV and the emission current was fixed at 20 mA. The UV–vis DRS spectra were collected using a Shimadzu UV-2550 spectrometer with BaSO₄ as the reference. Electron micrographs were taken by using a JEOL JEM-2010 transmission electron microscope operated at 200 kV. The elemental chemical states of the samples were examined by XPS using a Kratos-Axis Ultra DLD apparatus with an Al (mono) X-ray source and the binding energies of the samples were calibrated with respect to the signal for adventitious carbon (284.55 eV). The fourier transform infrared (FT-IR) spectra were collected using a Bruker Vector FT-IR spectrometer (6700) with a high-sensitivity micro-channel detector which was cooled by liquid N₂. Transient-state PL (TS-PL) spectra were recorded with a single photon counting spectrometer from (Edinburgh Instrument, FLS 920) with 1 μ s pulse lamp as the excitation. The steady-state PL spectra were measured with a PE LS 55 spectrofluoro-photometer at excitation wavelength of 390 nm.

The atmosphere-controlled SS-SPS measurement was carried out by using a home-built apparatus equipped with a lock-in amplifier (SR830) and synchronized with a light chopper (SR540). The sample was sandwiched between two indium tin oxide (ITO) glass electrodes and irradiated through a 500 W xenon lamp (CHF XQ500 W, Global xenon lamp power) to obtain a monochromatic light by passing through a double prism monochromator (SBP300). The transient-state surface photovoltage (TS-SPV) responses of the samples were measured in air atmosphere at room temperature. In a typical measurement, the sample chamber was connected to an ITO glass at the top electrode and a steel substrate at bottom electrode, and a thick mica spacer was placed between the ITO glass and the sample to decrease the space charge region at the ITO-sample interface. The samples were excited by a radiation pulse of 355 nm with 10 ns width from the second harmonic of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Lab-130-10H, Newport, Co.). The signals were amplified with a pre-amplifier and registered with a 1 GHz digital phosphor oscilloscope (DPO 4104B, Tektronix).

2.8. Electrochemical reduction measurement

The electrochemical reduction measurement in this work was operated using a traditional three-electrode system. The working electrode was a glassy carbon electrode of 0.3 cm in diameter. The

saturated calomel electrode was used as the reference electrode and a Pt sheet was used as the counter electrode. The electrolyte used in our test was 0.5 M NaClO₄. First, 5 mg of different samples mixed with 20 μ L of 5 wt % Nafion ionomer was dissolve in 0.18 mL ethanol aqueous solution. Then the catalyst ink was ultrasonicated for 30 min, and a suitable mass of the ink was dropped uniformly onto the clean GC electrode surface and then dried it in air. An AUTOLAB PG STAT101 electrochemical workstation was employed to test electrochemical activity. At the beginning, electrode potentials were cycled between two potential limits until perfectly overlapping, afterward we obtained the I–V curves. All the experiments were performed at room temperature.

2.9. Measurement of \cdot OH amount

In a typical measurement, 0.05 g of each sample was dispersed in a beaker containing 40 mL of 0.001 M coumarin solution. Prior to irradiation, the samples were stirred magnetically for 10 min to achieve adsorption-desorption equilibrium. The visible-light irradiation time for each sample was 1 h. After that, the sample was centrifuged and a certain amount of the pellucid liquid was taken and transferred in a Pyrex glass cell for the measurement of 7-hydroxycoumarin with characteristic emission peak at 460 nm through a spectrofluorometer (Perkin-Elmer LS55).

2.10. Evaluation of photocatalytic activity for H₂ evolution

The H₂ evolution was tested under visible-light ($\lambda > 400$) to evaluate the photocatalytic activities of the samples. The experiments were performed in a 250 mL quartz cell. For each experiment, 0.1 g of the sample was put in a mixture of 80 mL deionized water and 20 mL of methanol (sacrificial agent). A 300 W xenon lamp was used as the visible-light irradiation source, and the sample was irradiated in a closed water circulating system for 4 h. The amount of evolved H₂ was detected with an online TCD gas chromatograph (Tech, GC-9700, nitrogen gas carrier). The stability and recyclability tests were measured for 30 h, with a 5-h run cycle. For each run, the sample was dried and irradiated under visible-light.

2.11. Evaluation of photocatalytic activity for CO₂ reduction

In the photocatalytic reduction of CO₂, 0.2 g of the sample was dispersed in 8 mL water (with or without 2 mL methanol) and the solution was contained in a cylindrical steel reactor with 100 mL volume and 3.5 cm² area. Then high purity CO₂ gas was bubbled in the reactor after passing through water for reaching ambient pressure. Then the CO₂/H₂O system was equilibrated for 1 h and a 300 W xenon lamp was used as the light source with a cut-off filter of 420 nm for the photocatalytic reaction. After irradiation for 8 h, continually 0.5 mL of gas was taken from the reaction cell at given time interval for the analysis of CH₄ concentration using a gas chromatograph (GC-2014 with FID detector; Shimadzu Corp., Japan). A gas chromatography-mass spectrometer (MS5977A, America Aligent) was employed for the analysis of CD₄ concentration to performe the isotopic experiments about CO₂ reduction with H₂O changed to D₂O.

3. Results and discussion

3.1. Structural characterization

According to the X-ray diffraction (XRD) patterns (Fig. S1), it is confirmed that the peaks at $2\theta = 13.1^\circ$ and 27.4° can be indexed to (100) and (002) diffraction planes of g-C₃N₄ [36]. A new peak appears at $2\theta = 25.2^\circ$ after coupling TiO₂ which belongs to anatase TiO₂ [37]. Moreover, two additional peaks appearing at $2\theta = 38.1^\circ$ and 44.2° after decorating Ag can be indexed to (111) and (200) facets of Ag [38]. One can notice that the related XRD peaks become strong with increasing

the amount of Ag or TiO_2 . Interestingly, the XRD pattern of 0.25 Ag/6 T/g- C_3N_4 clearly demonstrates that metallic Ag and anatase TiO_2 are successfully co-modified on g- C_3N_4 . UV-vis DRS (Fig. S2) show that the bandgap of g- C_3N_4 is hardly changed after coupling TiO_2 and decorating Ag, while a neglectable optical absorption appears in the visible-light region presumably due to the plasmonic effect of nano-sized Ag [39].

The surface composition and chemical state of the elements in the prepared samples are investigated by the X-ray photoelectron spectroscopy (XPS) (Fig. S3). For all samples, the typical peaks of C 1s and N 1s are in good agreement with the previous reports [40]. In particular, the peaks in XPS spectra of Ag $3d_{3/2}$ and Ag $3d_{5/2}$ are observed at 368.3 and 374.3 eV for 0.25 Ag/g- C_3N_4 and 0.25 Ag/6 T/g- C_3N_4 samples, indicating the existence of Ag^0 [41]. Moreover, the strong peaks of Ti 2p located at 458.5 (Ti $2p_{3/2}$) and 464.2 eV (Ti $2p_{1/2}$) and O 1s located at energy of 529.8 eV (the crystal lattice oxygen) are observed in the samples of 6 T/g- C_3N_4 and 0.25 Ag/6 T/g- C_3N_4 which means the existence of TiO_2 [20,42]. In addition, one can see from the O 1s spectrum that the peak of the crystal lattice oxygen is not found in the Ag-decorated g- C_3N_4 .

Transmission electron microscopy (TEM) images were taken to characterize the morphology and measure the size of the as-prepared hybrid structures. As seen in Figs. 1A and S4, the g- C_3N_4 is sheet-like structure, the diameters of TiO_2 and Ag nanoparticle are estimated to be ~ 5 nm and ~ 18 nm, respectively. It is noticed that the distances between the adjacent lattices are determined to be 0.352 and 0.236 nm, respectively, corresponding to the (101) plane of anatase TiO_2 and the (111) plane of Ag [43,44]. Thus, anatase TiO_2 and metallic Ag are successfully co-modified on g- C_3N_4 with close contacts. This is in good agreement with the XRD results.

3.2. Photogenerated charge separation and lifetime

To investigate the photogenerated charge properties of the samples, the surface photovoltage technique including steady-state surface photovoltage spectroscopy (SS-SPS), TS-SPV responses and PL spectra were employed. In general, the stronger is the SS-SPS response, the higher is the charge separation. It is confirmed from the SS-SPS responses and PL spectra (Fig. S5 and S6A) that the photogenerated charge separation of g- C_3N_4 could be enhanced a lot after coupling a proper amount of TiO_2 , while enhanced a little after decorating a proper amount of Ag. Interestingly, the co-modified g- C_3N_4 (0.25 Ag/6 T/g- C_3N_4) displays the rather strong SS-SPS response, indicating the much high photogenerated charge separation.

To compare the separation and lifetime of the photogenerated

charges, the TS-SPV responses of g- C_3N_4 , 6 T/g- C_3N_4 , 0.25 Ag/g- C_3N_4 and 0.25 Ag/6 T/g- C_3N_4 were measured to further reveal the photo-generated charge property. As shown in Fig. 1B, it is noted from the intensities of the TS-SPV responses that the charge separation situation is consistent with the SS-SPS results. Moreover, the quantitative study of carrier dynamics usually provides further understanding of photo-generated charge properties of the photocatalysts. One can see that the photovoltage signals quickly climb to the maximum in the photovoltage spectra [45]. Then, the spatially dependent recombination between the free charges and localized centers by the diffusion process obeys the logarithmic law [46]. As seen in the Fig. 1B, all the TS-SPV decay profiles are well fitted by an exponential function. According to the fitted time constants of different samples, it is confirmed that the charge lifetime of g- C_3N_4 could be greatly prolonged after coupling TiO_2 , while it is not obvious after decorating Ag. Notably, the fitted time constant of 1065 μs in 0.25 Ag/6 T/g- C_3N_4 is around $\sim 100 \mu\text{s}$ long compared to that of g- C_3N_4 . In general, the long charge lifetime by the surface photovoltage response corresponds to the efficient photogenerated charge separation.

Further measurements of the PL lifetimes are conducted to explore the charge transfer from the g- C_3N_4 by TS-PL spectra. Fig. 2 shows the normalized TS-PL kinetics of g- C_3N_4 , 6 T/g- C_3N_4 , 0.25 Ag/g- C_3N_4 and 0.25 Ag/6 T/g- C_3N_4 . The TS-PL decay profiles for g- C_3N_4 were observed to have two distinct decay components: the initial fast decay over 1 μs , and a slow decay over 10 μs , in consistent with the recent reports [47]. As well known, the electron transfer from g- C_3N_4 to TiO_2 or Ag is energetically favorable. From the decay curves (Fig. 2 and Table. S1), it is shown that the decay lifetime of g- C_3N_4 is decreased after coupling TiO_2 or after decorating Ag, and it is much obvious for the coupled TiO_2 . The shortened PL decays mean that the electron transfer adds another decay channel to the excited states of g- C_3N_4 , in consistent with our considerations that the photogenerated charge separation of g- C_3N_4 could be enhanced after modifying with a proper amount of Ag and TiO_2 . In this case, the photogenerated electrons in g- C_3N_4 can be timely extracted, thus lowering the fast recombination. This is in good agreement with the TS-SPV results for the lowered fast recombination will provide more electrons to participate in generating the TS-SPV signal.

It is generally accepted that the amount of produced hydroxyl radicals ($\cdot\text{OH}$) can reflect the separation of photogenerated charges in the photocatalytic process [48]. Thus, it is meaningful to test the $\cdot\text{OH}$ amount to further verify the charge separation in a photochemical sense. Since the coumarin easily reacts with $\cdot\text{OH}$ to produce luminescent 7-hydroxy-coumarin, the coumarin fluorescent method is often utilized to measure the $\cdot\text{OH}$ amount. The fluorescence intensity related to the amounts of produced $\cdot\text{OH}$ for different C_3N_4 -based samples are

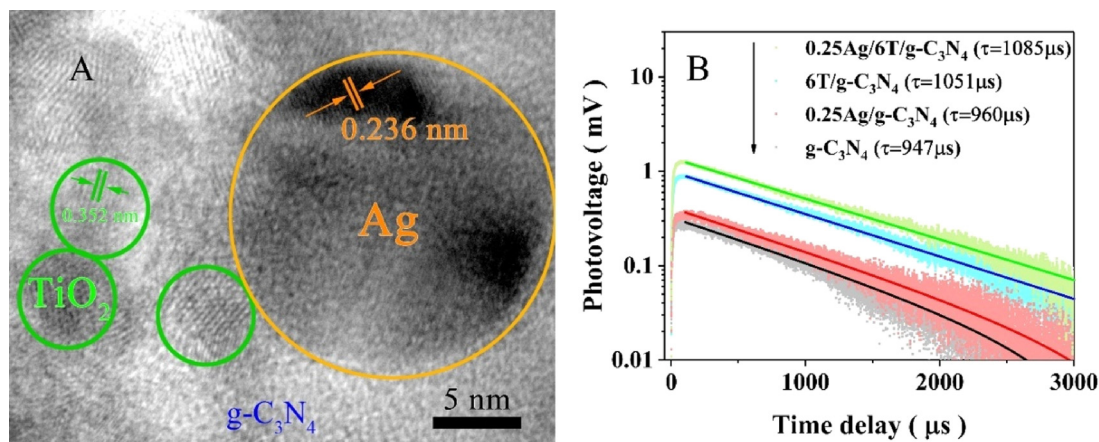


Fig. 1. High-resolution transmission electron microscopy (HRTEM) image of 0.25 Ag/6 T/g- C_3N_4 sample (A). Transient-state surface photovoltage (TS-SPV) responses of g- C_3N_4 , 0.25 Ag/g- C_3N_4 , 6 T/g- C_3N_4 and 0.25 Ag/6 T/g- C_3N_4 samples (B). xT/g- C_3N_4 means TiO_2 coupled g- C_3N_4 in which x is the mass ratio percentage of TiO_2 to g- C_3N_4 in theory. yAg/g- C_3N_4 means Ag decorated g- C_3N_4 in which y is the mole ratio percentage of Ag to g- C_3N_4 in theory.

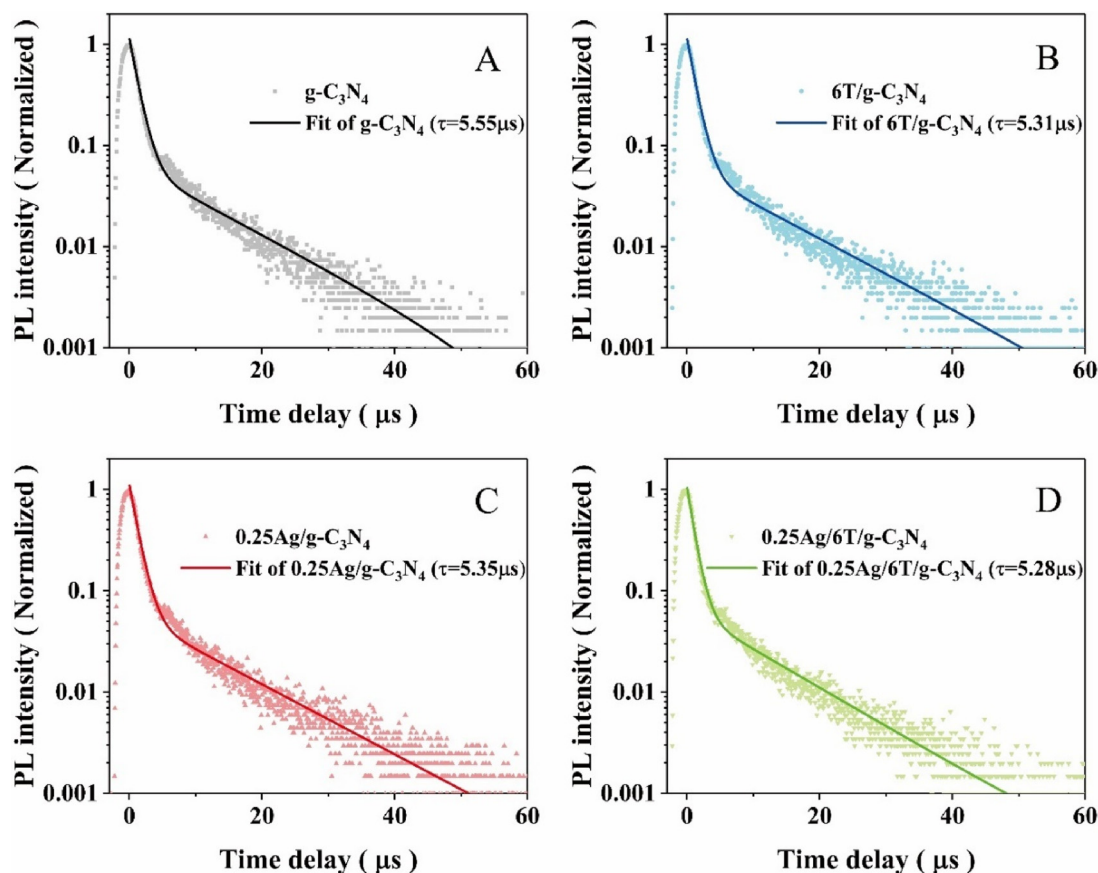


Fig. 2. Transient-state photoluminescence spectra of g-C₃N₄, 0.25 Ag/g-C₃N₄, 6 T/g-C₃N₄ and 0.25 Ag/6 T/g-C₃N₄ samples with 420 nm laser excitation.

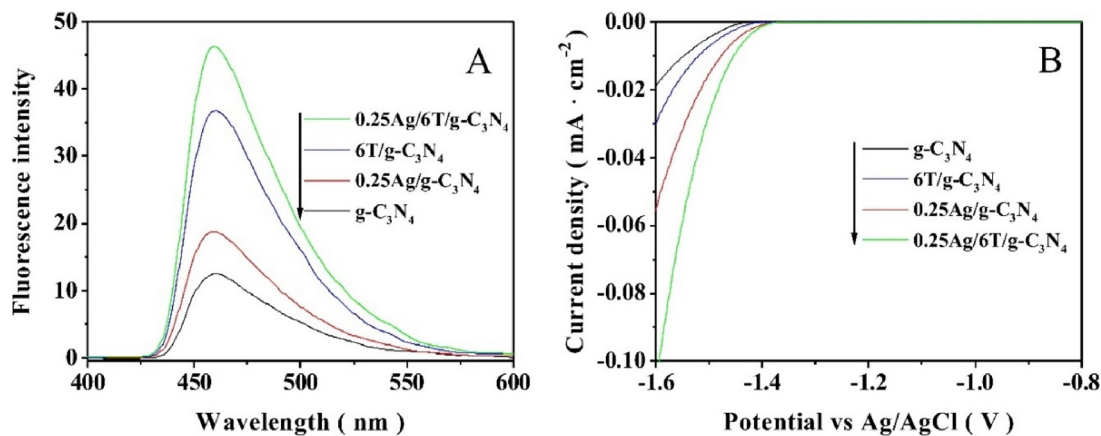


Fig. 3. Hydroxyl radical amount-related fluorescence spectra (A) and electrochemical I–V curves in the N₂ atmosphere (B) of g-C₃N₄, 0.25 Ag/g-C₃N₄, 6 T/g-C₃N₄ and 0.25 Ag/6 T/g-C₃N₄ samples.

shown in Fig. 3A. As expected, one can see that the observed fluorescence intensity order is as follows: g-C₃N₄ < 0.25 Ag/g-C₃N₄ < 6 T/g-C₃N₄ < 0.25 Ag/6 T/g-C₃N₄, which is well agreeable with the above photophysical results. Therefore, it is clearly demonstrated that the separation and lifetime of photogenerated charges on g-C₃N₄ are increased after coupling anatase TiO₂ and decorating metallic Ag, and it is much obvious for the coupled TiO₂ compared for the decorated Ag. Interestingly, the separation and lifetime of photogenerated charges on g-C₃N₄ could be increased greatly after co-modifying TiO₂ and Ag.

3.3. Evaluation of photocatalytic activities

To compare the catalytic property for H₂ evolution, electrochemical

reduction curves were recorded (Fig. 3B). The observed cathode current in the range of −1.6 V to −1.3 V versus Ag/AgCl is attributed to the water reduction for H₂ evolution [49,50]. It is shown that 6 T/g-C₃N₄ and 0.25 Ag/g-C₃N₄ are favorable for electrochemical H₂ evolution compared with g-C₃N₄, while it is much marked for 0.25 Ag/g-C₃N₄. In particular, the catalytic property of co-modified g-C₃N₄ is the best, indicating that it is much beneficial for water reduction.

As seen from the photocatalytic data (Fig. S7), the visible-light photocatalytic activity of g-C₃N₄ for H₂ evolution in the presence of methanol is improved after coupling a proper amount of TiO₂ and decorating a proper amount of Ag, respectively, and it is much obvious for the resulting 6 T/g-C₃N₄ and 0.25 Ag/g-C₃N₄. Unexpectedly, the photoactivity of 0.25 Ag/g-C₃N₄ is higher than that of 6 T/g-C₃N₄,

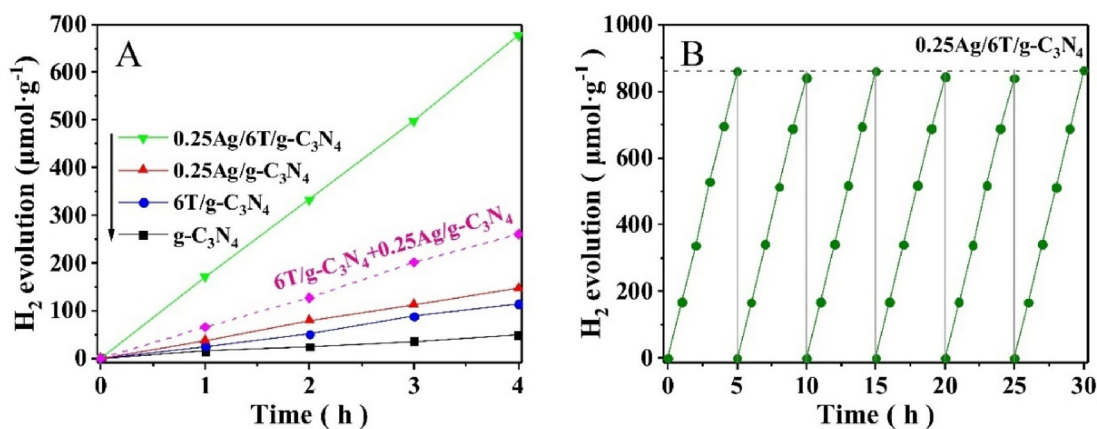


Fig. 4. Visible-light photocatalytic activities for H_2 evolution on $g\text{-C}_3\text{N}_4$, 0.25 A g/ $g\text{-C}_3\text{N}_4$, 6 T/ $g\text{-C}_3\text{N}_4$ and 0.25 A g/6 T/ $g\text{-C}_3\text{N}_4$ samples (A). Stability test of 0.25 A g/6 T/ $g\text{-C}_3\text{N}_4$ during the photocatalytic H_2 evolution for 30 h (B).

which is consistent with the catalytic property for H_2 evolution, while different from the photogenerated charge separation and lifetime. This illustrates that it is much important for efficient photocatalysis on $g\text{-C}_3\text{N}_4$ to improve the catalytic property for H_2 evolution compared to increase the photogenerated charge separation and lifetime. Interestingly, the visible-light photoactivity of 0.25 Ag/6 T/ $g\text{-C}_3\text{N}_4$ exhibits boost improvement as compared to bare $g\text{-C}_3\text{N}_4$ (Fig. 4A), even much higher than the sum of 6 T/ $g\text{-C}_3\text{N}_4$ and 0.25 Ag/ $g\text{-C}_3\text{N}_4$. This clearly reveals that there is an unexpected synergistic effect of prolonging the charge lifetime and providing the catalytic function for efficiently photocatalytic H_2 evolution on $g\text{-C}_3\text{N}_4$. In addition, the quantum efficiency of 0.25 Ag/6 T/ $g\text{-C}_3\text{N}_4$ under the single-wavelength (420 nm) irradiation is 1.73% which is much higher than the pure $g\text{-C}_3\text{N}_4$ (0.30%) (Supporting Information), and the photocatalytic recyclable test of 0.25 Ag/6 T/ $g\text{-C}_3\text{N}_4$ for 6 runs during the photocatalytic H_2 evolution (Fig. 4B) reveals that it is stable.

3.4. Discussion on mechanism

Based on the above results, it is indicated that the main role of the coupled TiO_2 as the new energy platform is to prolong the lifetime of photogenerated electrons with proper thermodynamic energy of $g\text{-C}_3\text{N}_4$, consequently leading to the enhanced charge separation, while the decorated Ag mainly works as a cocatalyst to improve the catalytic capability for H_2 evolution. Hence, it is believable that the synergistic effect of prolonging the charge lifetime and providing the catalytic function is well responsible for the exceptional visible-light photocatalytic activity of 0.25 Ag/6 T/ $g\text{-C}_3\text{N}_4$ for H_2 evolution. Similar to the coupled TiO_2 , the decorated Ag could also accept the photogenerated electrons of $g\text{-C}_3\text{N}_4$ so as to enhance the charge separation. However, the effect on the charge separation is weak for the decorated Ag compared with the coupled TiO_2 based on the above photophysical and photochemical results. This is possibly attributed to the low Fermi energy of Ag so that the transferred electrons possess low thermodynamic energy. Further, it would not be favorable for the transferred electrons to induce reduction reactions for H_2 evolution, even at the aid of catalytic function.

To further confirm the above points, we have carried out similar investigations by replacing Ag with Au and Pt. By means of XRD patterns and XPS spectra, it is confirmed that the metallic Au and Pt with the same amount as Ag are employed to modify $g\text{-C}_3\text{N}_4$ (Figs. S8A, S8B, S9A and S9B) [3,22,23,51]. Likewise, one can see from the UV–vis DRS results that the bandgap of $g\text{-C}_3\text{N}_4$ is almost unchanged after coupling TiO_2 and decorating Au or Pt (Figs. S8C and S9C). As shown from the SS-SPV, PL and TS-SPV results (Figs. S6B, S6C, S8D, S8E, S9D, S9E and Table 1), it is confirmed that the charge separation is increased and the charge lifetime is prolonged after decorating Au or Pt. As expected, it is

Table 1

TS-SPV lifetimes (τ_{TPV}), average transient-state PL lifetimes (τ_{PL}) and rates of evolved H_2 by visible-light photocatalysis on different samples (R_{H_2}), along with the rate ratios of evolved H_2 on metal/ TiO_2 / $g\text{-C}_3\text{N}_4$ to on TiO_2 / $g\text{-C}_3\text{N}_4$ (RR).

Different samples	τ_{TPV} (μs)	τ_{PL} (μs)	R_{H_2} ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	RR
$g\text{-C}_3\text{N}_4$	947	5.55	12.15	
6 T/ $g\text{-C}_3\text{N}_4$	1051	5.31	28.38	
0.25 A g/ $g\text{-C}_3\text{N}_4$	960	5.35	36.79	4.6
0.25 A g/6 T/ $g\text{-C}_3\text{N}_4$	1085	5.28	169.46	
0.25 Au/ $g\text{-C}_3\text{N}_4$	971	5.19	80.37	2.7
0.25 Au/6 T/ $g\text{-C}_3\text{N}_4$	1116	5.08	215.63	
0.25 Pt/ $g\text{-C}_3\text{N}_4$	1009	5.10	253.68	2.0
0.25 Pt/6 T/ $g\text{-C}_3\text{N}_4$	1195	5.03	519.73	

the most obvious for the TiO_2 -noble metal co-modified one. From the electrochemical reduction tests and the photocatalytic activities for H_2 evolution, one can see that the catalytic property and the visible-light activity for H_2 evolution could be improved after decorating Au or Pt. The H_2 -evolution activity is greatly improved after introducing TiO_2 and decorating a noble metal, even much higher than the sum of 6 T/ $g\text{-C}_3\text{N}_4$ and 0.25metal/ $g\text{-C}_3\text{N}_4$ samples (Table 1 and Fig. S12). This further demonstrates that it is much feasible to develop efficient photocatalysis for H_2 evolution on $g\text{-C}_3\text{N}_4$ by utilizing the synergistic effect confirmed above.

Particularly, one can notice that the visible-light photoactivities of metal-decorated $g\text{-C}_3\text{N}_4$ for H_2 evolution are improved after introducing a proper amount of anatase TiO_2 , with different improvement times as follows (Table 1): 4.6 (Ag) > 2.7 (Au) > 2.0 (Pt), and it is much marked for the Ag-decorated one. Differently, it is generally acceptable, also according to the electrochemical reduction results (Fig. S12), that the catalytic functions for H_2 evolution of decorated Ag, Au and Pt are gradually increased. Based on the TS-PL spectra (Figs. S10, S11, Tables S2, S3), it is confirmed that the decorated noble metal could easily accept the photogenerated electrons from $g\text{-C}_3\text{N}_4$, especially for the decorated Pt with the shorten TS-PL lifetime. However, the transferred electrons onto the decorated noble metal would quickly relax to the low Fermi energy level. Since the Fermi energy level of decorated noble metal is rather low, it is not feasible thermodynamically for the transferred electrons to induce the reduction reactions, consequently recombining with related holes. In this case, it is deduced that it is much beneficial for the decorated noble metal like Pt with good catalytic function to efficiently facilitate the transferred electrons with enough thermodynamic energy to initiate the reduction reactions. Thus, it is naturally understandable that it is much obvious for the confirmed synergistic effects of prolonging the charge lifetime and providing the catalytic function on efficient photocatalysis for H_2 evolution in the $g\text{-C}_3\text{N}_4$.

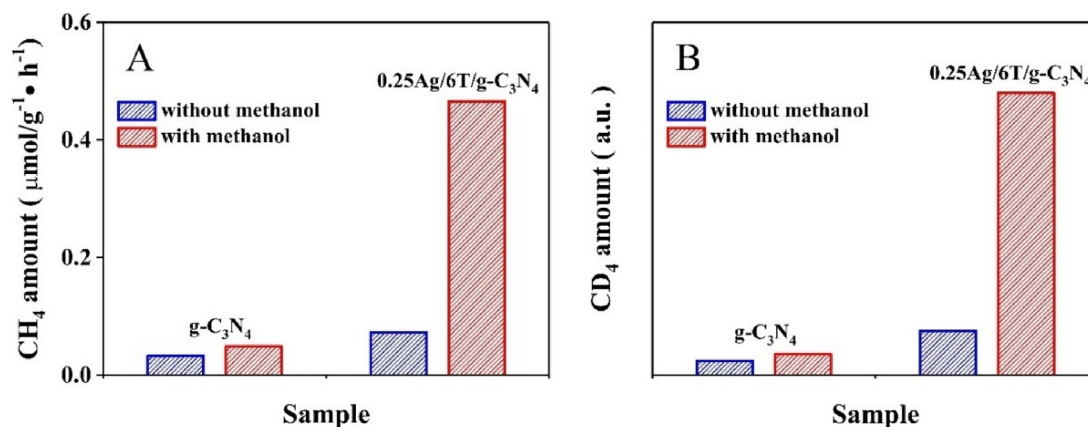
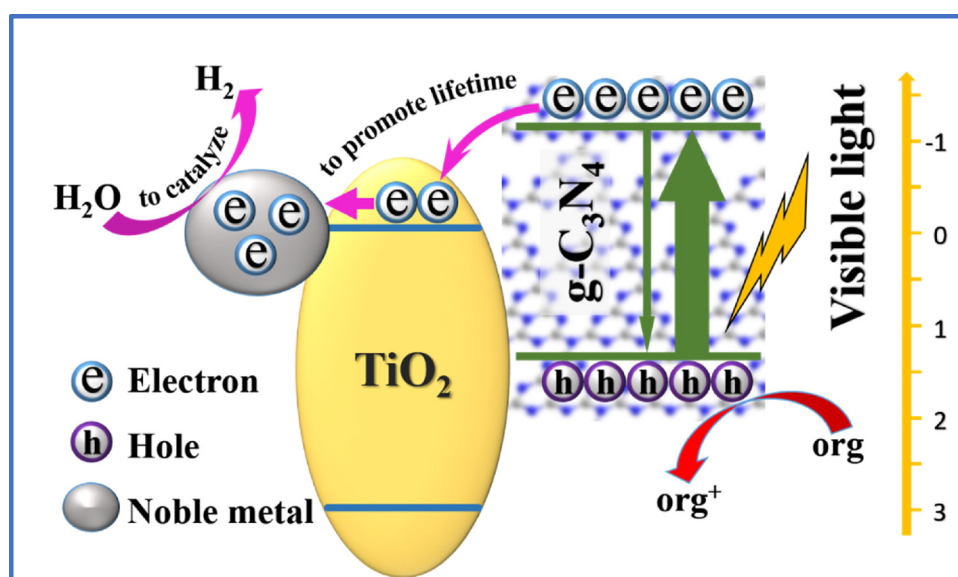


Fig. 5. Amounts of produced CH₄ (A) and CD₄ (B) from CO₂ reduction respectively in H₂O and D₂O on g-C₃N₄ and 0.25 Ag/6 T/g-C₃N₄ samples on the conditions of without and with methanol.



Scheme 1. Mechanism of the photogenerated charge transfer and induced photocatalytic processes for H₂ evolution in the presence of methanol under visible-light irradiation on g-C₃N₄ co-modified with noble metal and TiO₂.

C₃N₄ nanosheets co-modified with anatase TiO₂ and noble metal with weak catalytic function like Ag. In other words, it is much necessary for the excited electrons with proper-energy to prolong the lifetime for effectively catalytic processes to produce H₂.

In addition, the above-confirmed synergistic effects are further supported by the similar co-modification with Ag and nanocrystalline SnO₂. As shown in the Fig. S13, it is shown from the XRD patterns and UV–vis DRS results that the 0.25 Ag/6SnO₂/g-C₃N₄ sample is successfully synthesized [14,52]. According to the SS-SPS responses and the photocatalytic data, the observed results are similar to those of Ag and TiO₂ co-modified g-C₃N₄. This well indicates that the coupled SnO₂ could also act as the proper-energy platform to prolong the photogenerated charge lifetime, and then behave the synergistic effects with decorated Ag on efficient photocatalysis of g-C₃N₄ for H₂ evolution.

It is well established that methanol as an effective photogenerated hole capturer could be used to improve the photocatalytic activity for H₂ evolution. Meanwhile, it also provides free H⁺, which is favorable for electron-induced reduction reactions to produce H₂ thermodynamically. In this case, it is expected that one evolved H₂ is formed by two produced ·H radicals, and the produced ·H radicals mainly come from the reduction of H⁺ as a product of methanol oxidation other than from the adsorbed H₂O. To prove the expectation about the H resource of evolved H₂ by photocatalysis, an isotope experiment of

photocatalytic CO₂ reduction in D₂O has been designed to complete under the identical conditions since the produced ·D radicals would not enter into methane as the reduction production of CO₂. Gas chromatograph (GC) and gas chromatography-mass spectrometer (GC–MS) techniques were used to measure the amounts of CH₄ in H₂O and of CD₄ in D₂O (Fig. 5), respectively. One can see from Fig. 5A that the amounts of produced CH₄ in H₂O on g-C₃N₄ and 0.25 Ag/6 T/g-C₃N₄ are increased after adding methanol, respectively by ~1.48 and ~6.38 times. As shown in Figs. 5B and S14, the amounts of produced CD₄ in D₂O on g-C₃N₄ and 0.25 Ag/6 T/g-C₃N₄ are increased after adding methanol, respectively by ~1.44 and ~6.36 times. Unexpected, it is a surprisingly similar increase times of produced CH₄ or CD₄ amount on g-C₃N₄ or on 0.25 Ag/6 T/g-C₃N₄ after adding methanol, strongly indicating that the H resource of evolved H₂ by g-C₃N₄ nanosheet-based photocatalysis is mainly from the adsorbed H₂O other than the H⁺ through methanol oxidation. Interestingly, this is in good agreement with the literature, in which it is confirmed by the mean of the called operando nuclear magnetic resonance spectra [53]. This is also supported by the FT-IR spectra (Fig. S15), by which it is confirmed that all resulting g-C₃N₄-based photocatalysts exhibit good capacity to adsorb H₂O. In addition, it is obvious for visible-light photocatalytic CO₂ reduction to produce methane that the photoactivity of 0.25 Ag/6 T/g-C₃N₄ is much higher than that of g-C₃N₄ by 2.2-time improvement

without methanol and by 9.5-time improvement with methanol.

On the basis of above results and discussion, a simple mechanism schematic is proposed as Scheme 1. Firstly, g-C₃N₄ is excited by visible light to produce electron-hole pairs, and then the photogenerated holes are captured by CH₃OH to initiate oxidation reactions. Meanwhile, the photogenerated electrons transfer from the CB of g-C₃N₄ to the CB of TiO₂, leading to the lifetime increase of photogenerated electrons with proper thermodynamic energy. Subsequently, the transferred electrons further move onto the decorated noble metal, at which the induced reduction reactions with the adsorbed H₂O for H₂ evolution are catalyzed.

4. Conclusions

In summary, the photocatalytic activities of g-C₃N₄ nanosheets for H₂ evolution under visible-light irradiation have been greatly improved after coupling TiO₂ and then decorating a noble metal. The improved activity is attributed to the synergistic effect of prolonging the charge lifetime and catalyzing H₂ evolution. The prolonged charge lifetime is originated from the coupled TiO₂ for it could act as a proper-energy platform for accepting visible-light-excited electrons from g-C₃N₄. The catalyzing capability is originated from the decorated noble metal for it could act as the co-catalyst for H₂ evolution. Moreover, it is much necessary for the used noble metal cocatalyst with weak catalytic function like Ag for H₂ evolution to prolong the photogenerated charge lifetime. Moreover, it is clearly confirmed that the evolved H₂ mainly originates from the adsorbed water other than the disassociated H⁺ from methanol. This work provides new physical insights and feasible routes to develop efficient g-C₃N₄-based photocatalysts for energy production, and the confirmed synergistic effect is also applicable to other narrow-bandgap photocatalysts.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.05.034>.

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